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Osmadisiloxane and osmastannasiloxane complexes derived from silanolate complexes of osmium(II)

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Dedicated to Professor F.G.A. Stone, CBE, FRS, in celebration of his remarkable career and his continuing contributions to inorganic and organometallic chemistry

Abstract

Treatment of the five-coordinate chlorodimethylsilyl complex, $Os(SiMe_2Cl)Cl(CO)(PPh_3)_2$ with hydroxide readily produces $Os(SiMe_2OH)Cl(CO)(PPh_3)_2$ (1). Complex 1 is deprotonated by 'BuLi giving the silanolate complex, $Os(SiMe_2OLi)Cl(CO)(PPh_3)_2$ (2), which reacts further with Me₃SiCl or Me₃SnCl to give $Os(SiMe_2OSiMe_3)Cl(CO)(PPh_3)_2$ (3) or $Os(SiMe_2OSnMe_3)Cl(CO)(PPh_3)_2$ (4), respectively. The structures of 3 and 4 have been determined by X-ray crystallography. Reaction between $OsH(\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$ and $HSiMe_2Cl$ gives $Os(SiMe_2Cl)(\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$ (5). This six-coordinate chlorodimethylsilyl complex, is unreactive towards hydroxide at room temperature and at 60 °C forms $Os[Si(OH)_3](\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$ (6) upon chromatography on silica gel. Complex 6 is deprotonated by 'BuLi giving the intermediate silanolate complex, $Os(SiMe_2OLi)(\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$, which reacts further with Me_3SiCl to give $Os(SiMe_2OSiMe_3)(\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$ (8). Crystal structure determinations for 5, 6, 7, and 8 have been obtained and structural comparisons of these related compounds are made. © 2004 Elsevier B.V. All rights reserved.

Keywords: Osmadisiloxane complex; Silyl complex; Silanolate complex; Osmium; X-ray crystal structure

1. Introduction

Metallasilanols (L_nM –SiR₂OH) [1], like the non-metallated analogues, are likely to be valuable synthetic intermediates. Although these compounds are now well-characterised and available through two principal synthetic approaches (hydrolysis of halosilyl-ligands [1] or reaction between dimethyldioxirane and a ligated Si–H function [2]), the chemical reactivity associated with M–Si–OH linkages is mostly unexplored. Impor-

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tant results include the conversion of metallasilanols to both dimetalladisiloxanes (through condensation) [3] and to metalladisiloxanes [1b]. In one instance, the conversion of a metallasilanol to an isolated lithium metallasilanolate (L_nM -SiR₂OLi) has been reported and this was shown to be a dimer in the solid state [4].

The readily available five- and six-coordinate dimethylchlorosilyl–osmium(II) complexes, Os(SiMe₂Cl)Cl(CO)-(PPh₃)₂ and Os(SiMe₂Cl)(κ^2 -S₂CNMe₂)(CO)(PPh₃)₂, provided the opportunity to access through hydrolysis, the corresponding silanol complexes. We expected the accompanying set of ligands in these compound to constitute rather inert groupings and that, in effect, the "OsCl(CO)(PPh₃)₂" and "Os(κ^2 -S₂CNMe₂)(CO)(PPh₃)₂"

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fragments would provide unreactive and bulky substituents ("handles"), thus allowing focus on reactions at the Si centres. We describe herein: (i) the simple hydrolysis of Os(SiMe₂Cl)Cl(CO)(PPh₃)₂ to Os(SiMe₂OH)Cl(CO)- $(PPh_3)_2$ (1); (ii) the deprotonation of 1 to a solid lithium silanolate complex, Os(SiMe₂OLi)Cl(CO)(PPh₃)₂ (2); (iii) the reactions of 2 with Me₃SiCl or Me₃SnCl to give the corresponding osmadisiloxane, Os(SiMe₂OSiMe₃)-Cl(CO)(PPh₃)₂ (3), or osmastannasiloxane, Os(SiMe₂- $OSnMe_3)Cl(CO)(PPh_3)_2$ (4), respectively; (iv) synthesis of Os(SiMe₂Cl)(κ^2 -S₂CNMe₂)(CO)(PPh₃)₂ (5) and subsequent hydrolysis on silica gel to $Os(SiMe_2OH)(\kappa^2$ - $S_2CNMe_2)(CO)(PPh_3)_2$ (6); (v) the unusual reaction of 5 or 6 with KOH to give the trihydroxysilyl complex, $Os[Si(OH)_3](\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$ (7); (vi) the transformation of $Os(SiMe_2OH)(\kappa^2-S_2CNMe_2)(CO)$ - $(PPh_3)_2$ (6) through reaction with ^tBuLi followed by Me₃SiCl to give the osmadisiloxane, Os(SiMe₂OSi- Me_3)(κ^2 -S₂CNMe₂)(CO)(PPh₃)₂ (8); (vii) the crystal structures of 3-8.

2. Results and discussion

2.1. Preparation of $Os(SiMe_2OH)Cl(CO)(PPh_3)_2$ (1) and reaction of 1 with ^tBuLi

Treatment of an orange-yellow solution of Os(Si- Me_2Cl)Cl(CO)(PPh₃)₂ in THF with an aqueous solution of sodium hydroxide readily yields the yellow hydrolysis product, Os(SiMe₂OH)Cl(CO)(PPh₃)₂ (1) (see Scheme 1).

The IR spectrum of 1 shows a v(CO) band at 1910 cm⁻¹. As expected, this is lower than the corresponding band for Os(SiMe₂Cl)Cl(CO)(PPh₃)₂ which is found at 1917 cm⁻¹ in CH₂Cl₂ solution (the solid state spectrum, with bands at 1932, 1918, 1905 cm⁻¹, is complicated by solid-state splitting) [5]. In addition, the IR spectrum shows an absorption at 3626 cm⁻¹ which is assigned to v(OH). The ¹H NMR also reveals the presence of the Si–OH function with a resonance at 2.08 ppm which disappears on addition of D₂O. Other spectroscopic data for 1 and all other new compounds described herein are collected in Section 4.

The hydroxy function in 1 can be deprotonated with ^tBuLi (see Scheme 1) and an orange solid, formulated as $Os(SiMe_2OLi)Cl(CO)(PPh_3)_2$ (2), can be isolated. The IR spectrum of this orange solid shows a strong v(CO) band at 1876 cm⁻¹. This band position is strikingly lower than the v(CO) for 1 at 1910 cm⁻¹ but is appropriate for a lithium silanolate salt. This formulation is further supported by the reactions of 2 which are described in the following section. The only other compound of this type of which we are aware, is [Ir-(SiⁱPr₂OLi)HCl(PEt₃)₂]₂ [4], where X-ray crystallography shows that the dimer is held together by a four-membered Li₂O₂ ring. It is likely that the solid state structure of 2 also involves intermolecular associations involving lithium and oxygen but unfortunately we were unable to grow a suitable single crystal of 2 for X-ray analysis to verify this. All attempts to acquire solution NMR spectroscopic data for 2 were unsuccessful. Instead, because of the extreme moisture



Scheme 1. Synthesis and reactions of a five-coordinate silanolate complex of osmium(II).

sensitivity of **2**, data for the reprotonated compound **1** was always obtained.

2.2. Reactions of $Os(SiMe_2OLi)Cl(CO)(PPh_3)_2$ (2) with Me_3SiCl and Me_3SnCl and the crystal structures of the products, $Os(SiMe_2OSiMe_3)Cl(CO)(PPh_3)_2$ (3) and $Os(SiMe_2OSnMe_3)Cl(CO)(PPh_3)_2$ (4)

Treatment of 2 with either Me₃SiCl or Me₃SnCl produces in high yield the orange complexes, Os- $(SiMe_2 - OSiMe_3)Cl(CO)(PPh_3)_2$ (3) or $Os(SiMe_2OSn Me_3$)Cl(CO) (PPh_3)₂ (4), respectively (see Scheme 1). The physical properties for these two compounds are closely similar, both showing v(CO) in the IR spectra at 1892 cm⁻¹. This value is conspicuously lower than the value measured (1910 cm^{-1}) for the related hydroxysilyl compound 1, and can be attributed to the electron-releasing properties of the Me₃Si and Me₃Sn groups. In the ¹H NMR spectra the resonances for the osmium-bound SiMe₂ groups are at 0.27 ppm (for 3) and 0.19 ppm (for 4). The SiMe₃ signal in 3 is at -0.23 ppm and the SnMe₃ signal in 4 is at 0.02 ppm (with Sn satellites, ${}^{2}J_{SnH} = 56.8$ Hz). Although compounds with L_nM -Si-O-Si [3,1b] and L_nM -Sn-O-Si [6] linkages are known and structurally characterised, we are not aware of compounds containing the L_nM –Si–O–Sn linkage.

The crystal structures of 3 and 4 were determined and the molecular geometries are shown in Figs. 1 and 2, respectively. Crystal data pertaining to these structures and other structures reported in this paper are presented in Table 1. Selected bond lengths and angles for 3 and 4 are collected in Tables 2 and 3, respectively. Both 3 and 4 crystallise as 0.5 benzene solvates and are isostructural. The overall geometry about osmium is similar to that of other five-coordinate osmium silvl complexes, Os(silvl)Cl(CO)(PPh₃)₂ [7], and can be described as tetragonal pyramidal with the angle between the silvl ligand and the chloride opened to 104.33(6)° (compound 3) and to 104.52(10)° (compound 4). The Os-Si distances are 2.3613(11) (compound 3) and 2.3654(19) Å (compound 4). These are at the long end of the range of five-coordinate osmium-silicon bond lengths, the average for 14 observations being 2.3159 with a SD of 0.0283 Å (Cambridge Crystallographic Data Base). In compound 3 the two Si-O distances are almost identical (Si(1)-O(2) = 1.658(3)) and Si(2)-O(2) = 1.648(3) Å). In compound 4 the Si-O distance is shorter than those in 3 (Si–O(2) = 1.619(5) Å), and Sn-O(2) = 1.986(4) Å. The angles at the bridging oxygen for 3 and 4 are rather similar $(141.03(17)^{\circ})$ and 136.1(3)°, respectively).

2.3. Preparation and crystal structure of $Os(SiMe_2Cl)-(\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$ (5)

In Section 2.1 above it was shown that the chlorodimethylsilyl ligand in the five-coordinate complex, Os(SiMe₂Cl)Cl(CO)(PPh₃)₂, undergoes hydrolysis readily. To examine the reactivity, towards hydrolysis, of the chlorodimethylsilyl ligand when bound to osmium in a six-coordinate environment, the complex Os(Si-Me₂Cl)-(κ^2 -S₂CNMe₂)(CO)(PPh₃)₂ (5) was prepared. Following the successful route found for the synthesis of the closely related Ru(SiPh₂Cl)(κ^2 -S₂CNMe₂)-(CO)(PPh₃)₂ [8], OsH(κ^2 -S₂CNMe₂)(CO)(PPh₃)₂ was treated with HSiMe₂Cl to give pale yellow 5 in high yield (see Scheme 2). The IR spectrum of 5 shows



Fig. 1. Molecular geometry of Os(SiMe₂OSiMe₃)Cl(CO)(PPh₃)₂ (3).



Fig. 2. Molecular geometry of Os(SiMe₂OSnMe₃)Cl(CO)(PPh₃)₂ (4).

Table 1	
Data collection and processing parameters for 3-8	

	$3 \cdot 0.5 C_6 H_6$	$4 \cdot 0.5 \mathrm{C_6H_6}$	$\textbf{5}\cdot CH_2Cl_2$	6	$7 \cdot H_2O$	8
Formula	C45H48ClO2OsP2Si2	C45H48ClO2OsP2SiSn	C43H44Cl3NOOsP2S2Si	C42H43NO2OsP2S2Si	C40H39NO2OsP2S2Si	C ₄₅ H ₅₁ O ₂ OsP ₂ S ₂ Si ₂
Molecular weight	964.60	1055.2	1041.49	938.12	958.07	1010.31
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic
Space group	C2/c	C2/c	C2/m	$P\bar{1}$	$P\overline{1}$	$P\overline{1}$
a (Å)	35.3038(4)	35.2381(4)	28.0553(4)	11.3230(1)	11.1660(2)	11.3201(1)
b (Å)	10.6094(1)	10.6330(1)	15.1200(2)	13.2260(2)	12.7355(2)	12.3867(2)
<i>c</i> (Å)	24.5149(4)	24.5039(4)	11.4361(2)	16.0408(2)	14.8788(3)	17.4662(1)
α (°)				99.665(1)	94.656(1)	107.753(1)
β (°)	110.641(1)	110.550(1)	96.699(1)	105.329(1)	107.200(1)	93.567(1)
γ (°)				110.852(1)	102.977(1)	97.475(1)
$V(\text{\AA}^3)$	8592.68(19)	8562.04(17)	4829.40(13)	2071.54(4)	1944.66(6)	2299.14(4)
Ζ	8	8	4	2	2	2
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.491	1.637	1.432	1.504	1.636	1.459
<i>F</i> (000)	3880	4168	2080	940	956	1020
$\mu ({\rm mm}^{-1})$	3.19	3.75	3.01	3.32	3.54	3.02
Crystal size (mm)	$0.24 \times 0.18 \times 0.14$	$0.18 \times 0.16 \times 0.12$	$0.50 \times 0.28 \times 0.24$	$0.36 \times 0.22 \times 0.16$	$0.32 \times 0.20 \times 0.18$	$0.38 \times 0.20 \times 0.18$
$2\theta_{\min,\max}$ (°)	1.7, 26.4	1.78, 25.77	1.4, 26.4	1.7, 26.5	1.5, 26.5	1.8, 26.0
Reflections collected	39 136	23 771	27 924	19 157	18 381	21 409
Independent reflections (<i>R</i> _{int})	8795 (0.0477)	8165 (0.0473)	5113 (0.0143)	8308 (0.0144)	7952 (0.0146)	8908 (0.0150)
A _{min.max}	0.514, 0.663	0.552, 0.662	0.314, 0.532	0.381, 0.619	0.397, 0.568	0.393, 0.612
Goodness-of-fit on F^2	1.110	1.16	1.07	1.04	1.05	1.04
R (observed data)	$R_1 = 0.0328; wR_2 = 0.0661$	$R_1 = 0.0466; wR_2 = 0.0792$	$R_1 = 0.0240; wR_2 = 0.0685$	$R_1 = 0.0156; wR_2 = 0.0417$	$R_1 = 0.0165; wR_2 = 0.0425$	$R_1 = 0.0192; wR_2 = 0.0495$
R (all data)	$R_1 = 0.0448; wR_2 = 0.0706$	$R_1 = 0.0685; wR_2 = 0.0865$	$R_1 = 0.0244; wR_2 = 0.0688$	$R_1 = 0.0164; wR_2 = 0.0420$	$R_1 = 0.0172; wR_2 = 0.0428$	$R_1 = 0.0205; wR_2 = 0.0502$
Differential map (min, max) (e Å ⁻³)	-0.81, +1.91	-1.06, +0.82	-1.28, +1.05	-0.50, +0.65	-0.68, +0.59	-1.01, +1.82

 $\frac{|F_{\rm o}| - |F_{\rm c}|| / \sum |F_{\rm o}|}{|R = \sum ||F_{\rm o}| - |F_{\rm c}|| / \sum |F_{\rm o}|.}$ $wR_2 = \left\{ \sum [w(F_{\rm o}^2 - F_{\rm c}^2)^2] / \sum [w(F_{\rm o}^2)^2] \right\}^{1/2}.$

Table 3

Table 2

Selected bolid lengths (A) and angles () 101 3
Os–C(1′)	1.774(9)
Os–C(1)	1.774(7)
Os–Si(1)	2.3613(11)
Os–P(2)	2.3648(9)
Os–P(1)	2.3876(10)
Os-Cl	2.419(2)
Os–Cl′	2.449(3)
Si(1)–O(2)	1.658(3)
Si(1)–C(3)	1.872(5)
Si(1)–C(2)	1.874(5)
Si(2)–O(2)	1.648(3)
Si(2)–C(5)	1.859(4)
Si(2)-C(4)	1.861(4)
Si(2)–C(6)	1.864(5)
C(1)–Os–Si(1)	88.8(2)1
C(1)–Os–P(2)	90.9(2)
Si(1)–Os–P(2)	94.57(4)
C(1)–Os–P(1)	92.2(2)
Si(1)-Os-P(1)	98.05(4)
P(2) - Os - P(1)	167.05(4)
C(1)–Os–Cl	166.8(2)
Si(1)–Os–Cl	104.33(6)
P(2)–Os–Cl	87.37(5)
P(1)–Os–Cl	86.70(5)
O(2)-Si(1)-C(3)	104.20(18)
O(2)-Si(1)-C(2)	106.7(2)
C(3)-Si(1)-C(2)	105.3(3)
O(2)–Si(1)–Os	112.39(10)
C(3)-Si(1)-Os	115.80(18)
C(2)-Si(1)-Os	111.68(16)
O(2)–Si(2)–C(5)	108.01(17)
O(2)-Si(2)-C(4)	110.90(18)
C(5)-Si(2)-C(4)	108.3(2)
O(2)–Si(2)–C(6)	109.89(18)
C(5)–Si(2)–C(6)	110.8(2)
C(4)–Si(2)–C(6)	108.9(2)
Si(2)–O(2)–Si(1)	141.03(17)

v(CO) at 1888, 1869 cm⁻¹ (solid-state splitting). The ¹H NMR spectrum shows a singlet resonance at 0.29 ppm for the equivalent methyl groups on silicon and signals at 1.99 and 2.22 ppm for the two inequivalent methyl groups of the dimethyldithiocarbamate ligand. The ³¹P NMR shows a singlet resonance at 8.6 ppm and all of these data together are compatible with the structure having mutually *trans* triphenylphosphine ligands as depicted in Scheme 2 and as confirmed by the X-ray crystal structure determination described below.

The molecular geometry of **5** is shown in Fig. 3 with selected bond lengths and angles presented in Table 4. The attachment of the bidentate dimethyldithiocarbamate ligand is unsymmetrical, with the Os–S distance greater when S is *trans* to the silyl ligand (2.5159(9) Å) and less when S is *trans* to the CO ligand (2.4622(10) Å). This observation relates to the *trans* influence of the silyl ligand. The Os–Si distance in **5** is 2.4021(11)

Selected bond lengths (Å) and angles (°) for 4

	0 ()	6 ()	
Os-C(1')			1.753(14)
Os-C(1)			1.782(10)
Os-P(2)			2.3610(16)
Os–Si			2.3654(19)
Os-P(1)			2.3710(17)
Os-Cl			2.410(4)
Os–Cl′			2.450(5)
Si-O(2)			1.619(5)
Si-C(2)			1.858(7)
Si-C(3)			1.866(8)
Sn-O(2)			1.986(4)
Sn-C(4)			2.110(7)
Sn-C(5)			2.122(7)
Sn-C(6)			2.123(7)
O(1) - C(1)			1.174(13)
O(1') - C(1')			1.077(15)
			150.2(5)
C(1') - Os - C(1)			178.3(7)
C(1')–Os– $P(2)$			88.6(6)
C(1)–Os–P(2)			90.7(3)
$C(1') - Os - S_1$			93.0(6)
C(1) - Os - Si			88.6(4)
P(2) = Os = Si			93.21(6)
C(1') = Os = P(1)			88.6(6)
C(1)-Os- $P(1)$			91.7(3)
P(2) = Os = P(1)			168.16(6)
$S_1 - O_S - P(1)$			98.43(6)
C(1') = Os = C1			11.5(6)
C(1)–Os–Cl			166.8(4)
P(2)–Os–Cl			87.84(8)
SI-OS-CI			104.52(10)
P(1) = Os = CI			87.15(8)
C(1') - Os - Cl'			157.8(6)
C(1) = Os = CI'			20.5(4)
P(2)–Os–Cľ			88.29(11)
SI-OS-CI			109.07(15)
P(1)=Os=Cl'			89.95(11)
CI = Os = CI'			146.34(17)
O(2) - Si - C(2)			108.9(3)
$O(2) - S_1 - C(3)$			105.9(3)
$C(2) = S_1 = C(3)$			104.1(4)
$O(2) - S_1 - O_S$			110.77(18)
C(2)-Si-Os			110.5(3)
$C(3) = S_1 = O_S$			116.3(3)
O(2) - Sn - C(4)			107.6(3)
O(2) - Sn - O(5)			103.4(3)
C(4) = Sn = C(5)			112.6(3)
O(2) - Sn - O(6)			105.8(3)
C(4) = Sn = C(6)			111.3(3)
C(3) = Sn = C(6)			115.2(3)
51-O(2)-Sn			136.1(3)

Å, which is close to the average (2.4499 with SD 0.0508 Å) of 10 measured distances recorded in the Cambridge Crystallographic Data Base for octahedral osmium silyl complexes where silicon is 4-coordinate. The Si–Cl distance is 2.1223(16) Å, which is long when compared with the average of recorded Si–Cl distances of 2.0579 Å, SD 0.0435 Å (Cambridge Crystallographic Data Base). In contrast to the "flattening" of the organic substituents about silicon observed in the structure of



Scheme 2. Synthesis of a six-coordinate osmasilanol complex and conversion to an osmadisiloxane through the intermediacy of a proposed osmasilanolate complex.

 $Ru(SiPh_2Cl)(\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$ [8] the angles Os–Si–Me (116.52(8)°) and Os–Si–Cl (116.70(6)°) in **5** are closely similar.



Fig. 3. Molecular geometry of $Os(SiMe_2Cl)(\kappa^2-S_2CNMe_2)(CO)-(PPh_3)_2$ (5).

2.4. Hydrolysis reactions of $Os(SiMe_2Cl)(\kappa^2-S_2CN-Me_2)(CO)(PPh_3)_2$ (5): preparation and crystal structures of $Os(SiMe_2OH)(\kappa^2-S_2CNMe_2)(CO)-(PPh_3)_2$ (6) and $Os[Si(OH)_3](\kappa^2-S_2CNMe_2)(CO)-(PPh_3)_2$ (7)

The hydrolysis procedure which was successful for the conversion of Os(SiMe₂Cl)Cl(CO)(PPh₃)₂ to Os(Si-Me₂OH)Cl(CO)(PPh₃)₂ (aqueous NaOH in THF at room temperature) when applied to $Os(SiMe_2Cl)(\kappa^2 S_2CNMe_2)(CO)(PPh_3)_2$ gave only trace amounts of the hydrolysis product $Os(SiMe_2OH)(\kappa^2-S_2CNMe_2)(CO)$ -(PPh₃)₂ even with prolonged reaction times. Clearly, the reactivity of the Si-Cl bond in the chlorodimethylsilyl ligand is greatly reduced when it is bound in this six-coordinate complex rather than the five-coordinate complex, Os(SiMe₂Cl)Cl(CO)(PPh₃)₂. Using aqueous KOH in THF at a temperature of 60 °C for 16 h produced a 10% yield of Os(SiMe₂OH)(κ^2 -S₂CNMe₂)(CO)(PPh₃)₂ but the major product (36%) was, unexpectedly, the trihydroxysilyl complex, $Os[Si(OH)_3](\kappa^2-S_2CNMe_2)$ -(CO)- $(PPh_3)_2$ (7) (see Scheme 2). Another product of this reaction proved to be the hydride, $OsH(\kappa^2-S_2CNMe_2)$ -(CO)- $(PPh_3)_2$ (20%). If this high temperature reaction was left for a longer time the proportion of the hydride complex formed was observed to increase. An alternative synthesis of 7 involves treatment of the hydroxydimethylsilyl complex 6 with KOH using the same conditions as were successful for converting 5 to 7. It

Table 4 Selected bond lengths (Å) and angles (°) for **5**

Os–C(1)	1.845(4)
Os–P(1)	2.3884(7)
Os–Si	2.4021(11)
Os–S(2)	2.4622(10)
Os–S(1)	2.5159(9)
S(1)–C(2)	1.718(4)
S(2)–C(2)	1.712(4)
Si-C(5)#1	1.962(2)
Si–Cl(1)	2.1223(16)
O–C(1)	1.179(5)
N-C(2)	1.333(5)
C(1)–Os–P(1)	89.87(2)
C(1)–Os–P(1)#1	89.87(2)
P(1)–Os–P(1)#1	165.18(4)
C(1)–Os–Si	89.79(12)
P(1)–Os–Si	97.407(18)
P(1)#1–Os–Si	97.408(18)
C(1)–Os–S(2)	175.73(12)
P(1)–Os–S(2)	90.683(17)
P(1)#1–Os–S(2)	90.683(17)
Si–Os–S(2)	85.94(3)
C(1)–Os–S(1)	113.68(12)
P(1)–Os–S(1)	83.273(17)
P(1)#1–Os–S(1)	83.273(17)
Si–Os–S(1)	156.53(3)
S(2)–Os–S(1)	70.59(3)
C(5)#1–Si–C(5)	99.64(16)
C(5)#1–Si–Cl(1)	102.44(8)
C(5)–Si–Cl(1)	102.44(8)
C(5)#1–Si–Os	116.52(8)
C(5)–Si–Os	116.52(8)
Cl(1)–Si–Os	116.70(6)

Symmetry transformations used to generate equivalent atoms: #1 x, -y, z.

is unusual to observe cleavage of methyl groups from silyl ligands bound to transition metals. However, it is not without precedent in organosilicon chemistry, e.g., an early report describes the reaction of Me₃SiOSiMe₃ with KOH at high temperatures to give Me₃SiOSiMe₂(OH) and CH₄ [9]. A possibly related observation is that Cp*RhH₂(SiEt₃)₂ is converted to Cp*RhH₂(SiEt₃)[-Si(OEt)₃] through treatment with EtOH [10].

There are very few compounds with trihydroxysilyl functions which do not undergo rapid condensation reactions to give three-dimensional framework solids [11]. Stable examples, $RSi(OH)_3$, usually have a very bulky R group [12] but even then the solids are either layers or cage-like structures with complex H-bond networks. A discrete Si(OH)₃ group has been recognised as a ligand [3]. In the ¹H NMR spectrum of the trihydroxysilyl complex 7 a resonance is seen at 1.65 ppm integrating for three protons. This is assigned to the Si(OH)₃ group. The structure of this novel trihydroxysilyl complex is discussed below.

We discovered, serendipidously, that a simple and effective method for the hydrolysis of $Os(SiMe_2Cl)(\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$ involved passage of this compound down a silica gel column using acetone as eluent.



Fig. 4. Molecular geometry of $Os(SiMe_2OH)(\kappa^2-S_2CNMe_2)-(CO)(PPh_3)_2$ (6).

In this way $Os(SiMe_2OH)(\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$ (6) was produced in 83% yield. The ease with which this hydrolysis occurs on silica gel, in contrast to the lack of reactivity towards aqueous base discussed above, perhaps suggests that the hydrolysis is "acid-catalysed" on silica gel. The other product from this chromatographic procedure did not contain a silvl ligand and proved to be $OsCl(\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$ (yield 11%, see Scheme 2). Interestingly, an X-ray crystallographic study of this chloride derivative [13] revealed that unlike the hydride and silvl analogues, the chloride complex has a geometry with Cl trans to CO and with mutually cis triphenylphosphine ligands. The IR spectrum of Os(Si- Me_2OH)(κ^2 -S₂CNMe₂)(CO)(PPh₃)₂ shows a v(CO) at 1859 cm⁻¹, significantly lower than the value for the analogous chlorodimethylsilyl complex 5. v(OH) is seen at 3643 cm⁻¹. In the ¹H NMR spectrum a resonance at 0.51 ppm is assigned to the OH group. The crystal structures of these unusual hydroxysilyl complexes 6 and 7 are described below.

The molecular geometries of **6** and **7** are shown in Figs. 4 and 5 with selected bond lengths and angles presented in Tables 5 and 6. The structures have mutually *trans* triphenylphosphine ligands as depicted in Scheme 2. The attachment of the bidentate dimethyldithiocarbamate ligand is again unsymmetrical, with the Os–S distances being greater when S is *trans* to the silyl ligand (2.5449(5) for **6** and 2.5244(5) Å for **7**) and less when S is *trans* to the CO ligand (2.4812(5) for **6** and 2.4622(5) Å for **7**), reflecting the *trans* influence of the silyl ligand. The Os–Si distance in **6** is 2.4334(5), and in **7** is 2.3761(6) Å. Both values are close to the average (2.4499 with SD 0.0508 Å) of 10 measured distances

Table 6



Fig. 5. Molecular geometry of $Os[Si(OH)_3](\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$ (7).

Table 5 Selected bond lengths (Å) and angles (°) for ${\bf 6}$

Os-C(1)	1.846(2)
Os–P(1)	2.3855(5)
Os–P(2)	2.3891(5)
Os–Si	2.4334(5)
Os–S(2)	2.4812(5)
Os–S(1)	2.5449(5)
Si–O(2)	1.7125(15)
Si-C(2)	1.875(2)
Si–C(3)	1.899(2)
S(1)–C(4)	1.7297(19)
S(2)–C(4)	1.7184(19)
O(1)–C(1)	1.182(2)
N(1)-C(4)	1.330(3)
C(1)–Os–P(1)	88.37(6)
C(1)–Os–P(2)	90.69(6)
P(1)–Os–P(2)	167.542(17)
C(1)–Os–Si	91.47(6)
P(1)–Os–Si	95.238(18)
P(2)–Os–Si	97.205(18)
C(1)–Os–S(2)	175.14(6)
P(1)–Os–S(2)	91.853(16)
P(2)–Os–S(2)	90.135(16)
Si–Os–S(2)	83.674(17)
C(1)–Os–S(1)	114.70(6)
P(1)–Os–S(1)	83.313(16)
P(2)–Os–S(1)	85.805(16)
Si–Os–S(1)	153.680(17)
S(2)–Os–S(1)	70.143(15)
O(2)–Si–C(2)	100.25(10)
O(2)–Si–C(3)	104.62(10)
C(2)–Si–C(3)	105.36(12)
O(2)–Si–Os	110.72(6)
C(2)–Si–Os	113.25(8)
C(3)–Si–Os	120.45(8)

Os–C(1)	1.839(2)
Os–P(2)	2.3692(5)
Os-P(1)	2.3741(5)
Os–Si	2.3761(6)
Os–S(2)	2.4622(5)
Os-S(1)	2.5244(5)
Si-O(2)	1.6591(17)
Si–O(4)	1.6596(17)
Si–O(3)	1.6722(18)
S(1)–C(2)	1.717(2)
S(2)–C(2)	1.712(2)
O(1)–C(1)	1.170(3)
N(1)–C(2)	1.320(3)
C(1)–Os–P(2)	89.94(6)
C(1)–Os–P(1)	89.78(6)
P(2)–Os–P(1)	171.727(18)
C(1)–Os–Si	92.48(7)
P(2)–Os–Si	93.450(19)
P(1)–Os–Si	94.823(19)
C(1)–Os–S(2)	177.11(7)
P(2)–Os–S(2)	89.999(17)
P(1)–Os–S(2)	90.696(18)
Si–Os–S(2)	84.643(19)
C(1)–Os–S(1)	112.75(7)
P(2)–Os–S(1)	86.134(17)
P(1)–Os– $S(1)$	86.351(17)
Si–Os–S(1)	154.76(2)
S(2)-Os-S(1)	70.127(17)
O(2)–Si–O(4)	106.53(9)
O(2)–Si–O(3)	105.38(10)
O(4)–Si–O(3)	104.52(10)
O(2)–Si–Os	109.93(7)
O(4)–Si–Os	110.87(6)
O(3)-Si-Os	$118\ 81(7)$

recorded in the Cambridge Crystallographic Data Base for octahedral osmium silyl complexes where silicon is 4-coordinate. Significantly, the trihydroxysilyl derivative has the shorter Os–Si distance. The Si–OH distance in **6** is 1.7125(15) Å and the three Si–OH distances in **7** are 1.6591(17), 1.6596(17), 1.6722(18) Å. The Si–OH distance in **6** is clearly longer than those in **7** and indeed all these values are at the long end of the observed range of Si–O distances (the average of all reported Si–O distances for four-coordinate Si is 1.6295 (SD 0.0334) Å, Cambridge Crystallographic Data Base).

It is interesting to compare the Os–Si distance in 7 with the Os–Si distances measured in two other structurally characterised trihydroxysilyl derivatives of osmium. The Os–Si distance in five-coordinate Os[Si(OH)₃]Cl-(CO)(PPh₃)₂ is 2.319(2) Å [3] and the Os–Si distance in the corresponding dicarbonyl derivative, Os[Si(OH)₃]Cl-(CO)₂(PPh₃)₂ is 2.464(1) Å [14]. The value for 7 falls midway between these two extremes. The tightly-bound trihydroxysilyl ligand in Os[Si(OH)₃]Cl(CO)(PPh₃)₂ shows no hydrogen-bond interactions, but the trihydroxysilyl ligand bound at the considerably longer distance in Os[Si(OH)₃]Cl(CO)₂(PPh₃)₂ has two hydroxy functions on each silyl ligand involved in the formation

Table 7 Hydrogen bond distances (Å) and angles (°) for 7

O–H· · ·A	d(O-H)	$d(H \cdot \cdot \cdot A)$	$d(O \cdot \cdot \cdot A)$	$\angle (O - H \cdot \cdot \cdot A)$
$O(3)-H(3)\cdots O(5)$	0.84	2.05	2.789(4)	145.6
O(2)−H(2)···S(2)#1	0.84	2.63	3.4263(18)	159.6
$O(4)-H(4)\cdot\cdot S(2)\#1$	0.84	2.60	3.4264(17)	167.9

Symmetry transformations used to generate equivalent atoms: #1 -x + 1, -y, -z + 1.

of a dimeric unit through hydrogen-bonds to a pair of OH groups of the same ligand on an adjacent molecule. Complex 7 crystallises with a single water molecule. Two water molecules are associated with two molecules of complex 7 through a hydrogen-bond network which involves only one OH function of each of the trihydroxy-silyl ligands. In addition, the other two hydroxy functions form weak intermolecular hydrogen-bonds to a S atom of another adjacent molecule. The dimensions of these hydrogen-bond interactions for 7 are presented in Table 7. The O–O distance for the SiO– $H \cdots OH_2$ interaction is 2.789(4) Å which lies in the middle of the range observed for O– $H \cdots O$ hydrogen bonding (2.48–2.90 Å)[15]. The O–S distances for the weak SiO– $H \cdots S$ interactions are 3.4263(18) and 3.4264(17) Å.

2.5. Conversion of $Os(SiMe_2OH)(\kappa^2-S_2CNMe_2)(CO)-(PPh_3)_2$ (6) to $Os(SiMe_2OSiMe_3)(\kappa^2-S_2CNMe_2)-(CO)(PPh_3)_2$ (8) and the crystal structure of 8

The single hydroxy function in Os(SiMe₂OH)(κ^2 - $S_2CNMe_2)(CO)(PPh_3)_2$ is readily deprotonated through treatment with ^tBuLi (see Scheme 2). However, in this case attempts to isolate the lithium silanolate complex were unsuccessful. Nevertheless, treatment of the silanolate prepared in situ with Me₃SiCl gave (8) in high yield. Complex 8 is also obtained, although in lower yield, when 'BuLi is replaced by triethylamine. Colourless crystals of 8 have v(CO) at 1861 cm⁻¹ in the IR spectrum. This is very close to the v(CO) value observed for the immediate precursor, 6 (1859 cm⁻¹). The ¹H NMR spectrum shows singlet resonances for the Me₃Si function at -0.18 ppm and for the Me₂Si function at 0.0 ppm. An X-ray crystal structure determination for 8 was carried out and the molecular structure is depicted in Fig. 6. Selected bond lengths and angles are presented in Table 8. The overall arrangement of donor atoms about the osmium is the same as described above for complexes 5, 6 and 7. The Os-S distances and the Os-Si distance in 8 are almost identical to those found for the precursor complex, 6. The osmium-bound Si-O distance in 8 is 1.6779(19) and the terminal Si–O distance is 1.6238(19) Å. These values are significantly different, in contrast to the two corresponding values in complex 3. which were almost identical. The Si-O-Si angle in 8 is 143.32(13)°, close to the values found in 3 and 4 (141.03(17)° and 136.1(3)°, respectively).



Fig. 6. Molecular geometry of $Os(SiMe_2OSiMe_3)(\kappa^2-S_2CNMe_2)-(CO)(PPh_3)_2$ (8).

3. Conclusions

It has been demonstrated that the reactivity towards hydrolysis of chlorodimethylsilyl ligands bound to osmium(II) varies widely. Whereas the five-coordinate complex Os(SiMe₂Cl)Cl(CO)(PPh₃)₂ is readily hydrolysed at room temperature by aqueous base to Os(Si- $Me_2OH)Cl(CO)(PPh_3)_2$, the six-coordinate complex $Os(SiMe_2Cl)(\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$ resists base hydrolysis at room temperature, and high temperature reaction produces the trihydroxysilyl complex Os- $[Si(OH)_3](\kappa^2-S_2CNMe_2)(CO)(PPh_3)_2$. Os $(SiMe_2Cl)(\kappa^2 S_2CNMe_2)(CO)(PPh_3)_2$ is, however, readily hydrolysed by chromatography on silica gel. Both hydroxydimethylsilyl complexes are deprotonated by ^tBuLi, giving silanolate complexes but only Os(SiMe₂OLi)Cl(CO)(PPh₃)₂ could be isolated as a solid. The silanolate complexes react with Me₃SiCl and Me₃SnCl to give the expected osmadisiloxane (3 and 8) and osmastannasiloxane (4) complexes, respectively. Crystal structure determinations of 3, 4, 5, 6, 7, and 8 verify the formulations of the new compounds.

4. Experimental

4.1. General procedures and instruments

Standard laboratory procedures were followed as have been described previously [16]. The compounds $Os(SiMe_2Cl)Cl(CO)(PPh_3)_2$ [5] and $OsH(\kappa^2-S_2CNMe_2)(-CO)(PPh_3)_2$ [17] were prepared according to the literature methods.

Table 8 Selected bond lengths (Å) and angles (°) for **8**

$\begin{array}{llllllllllllllllllllllllllllllllllll$	Os–C(1)	1.840(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Os–P(2)	2.3775(6)
Os-Si(1) $2.4294(7)$ Os-S(1) $2.4744(6)$ S(1)-C(2) $1.716(3)$ S(1)-C(2) $1.727(2)$ Si(1)-O(2) $1.6779(19)$ Si(1)-C(5) $1.895(3)$ Si(1)-C(6) $1.899(3)$ Si(2)-O(2) $1.6238(19)$ Si(2)-C(8) $1.815(4)$ Si(2)-C(7) $1.820(5)$ Si(2)-C(7) $1.820(5)$ Si(2)-C(1) $1.183(3)$ N(1)-C(2) $1.332(3)$ N(1)-C(2) $1.332(3)$ N(1)-C(2) $1.332(3)$ N(1)-C(3) $1.470(4)$ C(1)-Os-P(2) $89.50(7)$ C(1)-Os-P(1) $89.93(7)$ P(2)-Os-P(1) $164.94(2)$ C(1)-Os-Si(1) $97.38(2)$ P(2)-Os-Si(1) $97.5(8)$ P(2)-Os-Si(1) $97.5(8)$ P(2)-Os-Si(1) $97.5(8)$ P(1)-Os-Si(1) $90.56(2)$ P(1)-Os-Si(1) $91.54(2)$ Si(1)-Os-S(1) $91.54(2)$ Si(1)-Os-S(1) $91.54(2)$ Si(1)-Os-S(1) $91.54(2)$ Si(1)-Os-S(2) $82.97(2)$ Si(1)-Os-S(2) $82.97(2)$ Si(1)-Os-S(2) $15.53(8)$ P(2)-Os-S(2) $154.72(2)$ Si(1)-Os-S(2) $105.43(12)$ O(2)-Si(1)-C(6) $103.26(15)$ O(2)-Si(1)-C(6) $103.26(15)$ O(2)-Si(1)-C(6) $103.26(15)$ O(2)-Si(1)-Os $11.5.97(17)$ O(2)-Si(2)-C(7) $110.03(17)$ C(5)-Si(1)-Os $113.97(10)$ O(2)-Si(2)-C(7) $107.31(19)$ O(2)-Si(2)-C(7) $107.31(19)$ O(2)-S	Os–P(1)	2.3871(6)
Os-S(1) $2.4744(6)$ Os-S(2) $2.5441(6)$ S(1)-C(2) $1.716(3)$ S(2)-C(2) $1.727(2)$ S(1)-O(2) $1.6779(19)$ S(1)-C(5) $1.895(3)$ S(1)-C(6) $1.899(3)$ S(2)-C(2) $1.6238(19)$ S(2)-C(7) $1.820(5)$ S(2)-C(7) $1.833(3)$ N(1)-C(1) $1.183(3)$ N(1)-C(2) $1.332(3)$ N(1)-C(3) $1.470(4)$ C(1)-Os-P(1) $89.950(7)$ C(1)-Os-P(1) $89.93(7)$ P(2)-Os-P(1) $164.94(2)$ C(1)-Os-P(1) $89.93(7)$ P(2)-Os-S(1) $97.38(2)$ P(1)-Os-S(1) $97.58(2)$ P(1)-Os-S(1) $97.58(2)$ P(1)-Os-S(1) $174.09(8)$ P(2)-Os-S(1) $90.56(2)$ P(1)-Os-S(2) $115.53(8)$ P(2)-Os-S(1) $90.56(2)$ P(1)-Os-S(2) $115.53(8)$ P(2)-Os-S(2) $83.70(2)$ P(1)-Os-S(2) $13.53(2)$ C(1)-Os-S(2) $154.72(2)$ S(1)-Os-S(2) $103.22(12)$ C(5)-S(1)-C(6) $103.22(12)$ C(5)-S(1)-C(6) $103.22(12)$ C(5)-S(1)-Os $119.78(10)$ C(6)-S(1)-Os $119.78(10)$ C(5)-S(1)-Os $119.78(10)$ C(5)-S(1)-Os $113.91(10)$ O(2)-S(2)-C(7) $114.2(3)$	Os–Si(1)	2.4294(7)
Os-S(2) $2.5441(6)$ $S(1)-C(2)$ $1.716(3)$ $S(2)-C(2)$ $1.727(2)$ $S(1)-O(2)$ $1.6779(19)$ $Si(1)-C(5)$ $1.899(3)$ $Si(2)-O(2)$ $1.6238(19)$ $Si(2)-C(7)$ $1.820(5)$ $Si(2)-C(7)$ $1.820(5)$ $Si(2)-C(7)$ $1.833(3)$ $N(1)-C(2)$ $1.332(3)$ $N(1)-C(1)$ $1.183(3)$ $N(1)-C(2)$ $1.332(3)$ $N(1)-C(4)$ $1.464(4)$ $N(1)-C(3)$ $1.470(4)$ $C(1)-Os-P(2)$ $89.50(7)$ $C(1)-Os-P(1)$ $89.75(8)$ $P(2)-Os-Si(1)$ $97.57(8)$ $P(2)-Os-Si(1)$ $97.57(8)$ $P(2)-Os-S(1)$ $97.57(2)$ $P(1)-Os-S(1)$ $91.54(2)$ $S(1)-Os-S(1)$ $91.54(2)$ $S(1)-Os-S(1)$ $91.54(2)$ $S(1)-Os-S(2)$ $15.53(8)$ $P(2)-Os-S(2)$ $15.53(8)$ $P(2)-Os-S(2)$ $15.47(22)$ $S(1)-Os-S(2)$ $15.47(22)$ $S(1)-Os-S(2)$ $15.47(22)$ $S(1)-Os-S(2)$ $105.43(12)$ $O(2)-Si(1)-C(5)$ $105.43(12)$ $O(2)-Si(1)-C(6)$ $103.22(12)$ $O(2)-Si(1)-Os$ $119.69(7)$ $O(2)-Si(1)-Os$ $119.79(10)$ $O(2)-Si(2)-C(7)$ $114.2(3)$ $O(2)-Si(2)-C(7)$ $114.2(3)$ $O(2)-Si(2)-C(9)$ $107.31(19)$ $O(2)-Si(2)-C(9)$ $107.31(19)$ $O(2)-Si(2)-C(9)$ $105.8(3)$ $Si(2)-O(2)-Si(1)$ $105.8(3)$ $Si(2)-O(2)-Si(1)$ $107.31(19)$ $O(2)-Si(2)-C(9)$ <	Os–S(1)	2.4744(6)
S(1)-C(2) $1.716(3)$ $S(2)-C(2)$ $1.727(2)$ $S(1)-O(2)$ $1.6779(19)$ $S(1)-C(5)$ $1.895(3)$ $S(1)-C(6)$ $1.899(3)$ $S(2)-C(2)$ $1.6238(19)$ $Si(2)-C(8)$ $1.815(4)$ $Si(2)-C(7)$ $1.820(5)$ $Si(2)-C(9)$ $1.906(5)$ $O(1)-C(1)$ $1.183(3)$ $N(1)-C(2)$ $1.332(3)$ $N(1)-C(4)$ $1.464(4)$ $N(1)-C(3)$ $1.470(4)$ $C(1)-Os-P(2)$ $89.50(7)$ $C(1)-Os-P(1)$ $89.93(7)$ $P(2)-Os-Si(1)$ $97.38(2)$ $P(2)-Os-Si(1)$ $97.38(2)$ $P(1)-Os-Si(1)$ $97.38(2)$ $P(1)-Os-Si(1)$ $97.5(8)$ $P(2)-Os-Si(1)$ $97.5(8)$ $P(2)-Os-S(2)$ $97.5(8)$ $P(1)-Os-S(1)$ $174.09(8)$ $P(2)-Os-S(2)$ $97.5(8)$ $P(1)-Os-S(2)$ $97.5(8)$ $P(1)-Os-S(2)$ $15.53(8)$ $P(2)-Os-S(2)$ $15.53(8)$ $P(2)-Os-S(2)$ $15.53(8)$ $P(2)-Os-S(2)$ $15.47(2)$ $S(1)-Os-S(2)$ $15.47(2)$ $S(1)-Os-S(2)$ $105.43(12)$ $O(2)-Si(1)-C(5)$ $105.43(12)$ $O(2)-Si(1)-C(5)$ $105.43(12)$ $O(2)-Si(1)-C(5)$ $105.43(12)$ $O(2)-Si(1)-Os$ $119.97(17)$	Os-S(2)	2.5441(6)
S(2) $-C(2)$ 1.727(2)Si(1) $-O(2)$ 1.6779(19)Si(1) $-C(5)$ 1.895(3)Si(1) $-C(6)$ 1.899(3)Si(2) $-O(2)$ 1.6238(19)Si(2) $-C(8)$ 1.815(4)Si(2) $-C(7)$ 1.820(5)Si(2) $-C(7)$ 1.820(5)Si(2) $-C(7)$ 1.833(3)N(1) $-C(1)$ 1.183(3)N(1) $-C(2)$ 1.332(3)N(1) $-C(4)$ 1.464(4)N(1) $-C(3)$ 1.470(4)C(1) $-Os -P(1)$ 89.50(7)C(1) $-Os -P(1)$ 89.50(7)C(1) $-Os -P(1)$ 164.94(2)C(1) $-Os -P(1)$ 164.94(2)C(1) $-Os -P(1)$ 164.94(2)C(1) $-Os -S(1)$ 97.5(8)P(2) $-Os -S(1)$ 97.5(8)P(2) $-Os -S(1)$ 97.5(8)P(2) $-Os -S(1)$ 97.5(8)P(2) $-Os -S(1)$ 91.54(2)Si(1) $-Os -S(1)$ 91.54(2)Si(1) $-Os -S(1)$ 91.54(2)Si(1) $-Os -S(1)$ 91.54(2)Si(1) $-Os -S(2)$ 82.97(2)Si(1) $-Os -S(2)$ 154.72(2)Si(1) $-Os -S(2)$ 105.43(12)O(2) $-Si(1) -C(5)$ 105.43(12)O(2) $-Si(1) -C(6)$ 103.22(12)C(5) $-Si(1) -C(6)$ 103.22(12)C(5) $-Si(1) -C(6)$ 103.22(12)C(5) $-Si(1) -Os$ 119.78(10)C(6) $-Si(1) -Os$ 119.78(1	S(1) - C(2)	1.716(3)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	S(2)-C(2)	1.727(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Si(1) - O(2)	1.6779(19)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Si(1) - C(5)	1.895(3)
$\begin{array}{ccccccc} 1 & 1.6238(19) \\ Si(2)-C(8) & 1.815(4) \\ Si(2)-C(7) & 1.820(5) \\ Si(2)-C(9) & 1.906(5) \\ O(1)-C(1) & 1.183(3) \\ N(1)-C(2) & 1.332(3) \\ N(1)-C(4) & 1.464(4) \\ N(1)-C(3) & 1.470(4) \\ C(1)-Os-P(1) & 89.50(7) \\ C(1)-Os-P(1) & 89.93(7) \\ P(2)-Os-P(1) & 164.94(2) \\ C(1)-Os-Si(1) & 97.38(2) \\ P(1)-Os-Si(1) & 97.5(8) \\ P(2)-Os-Si(1) & 97.5(8) \\ P(2)-Os-Si(1) & 97.67(2) \\ C(1)-Os-S(1) & 97.67(2) \\ C(1)-Os-S(1) & 91.54(2) \\ Si(1)-Os-S(1) & 91.54(2) \\ Si(1)-Os-S(2) & 83.70(2) \\ P(1)-Os-S(2) & 83.70(2) \\ P(1)-Os-S(2) & 83.70(2) \\ P(1)-Os-S(2) & 83.70(2) \\ P(1)-Os-S(2) & 82.97(2) \\ Si(1)-Os-S(2) & 154.72(2) \\ Si(1)-Os-S(2) & 105.43(12) \\ O(2)-Si(1)-C(5) & 105.43(12) \\ O(2)-Si(1)-C(6) & 103.22(12) \\ C(5)-Si(1)-C(6) & 103.22(12) \\ O(2)-Si(1)-C(6) & 103.22(12) \\ O(2)-Si(1)-C(6) & 119.78(10) \\ C(6)-Si(1)-Os & 119.78(10) \\ C(6)-Si(2)-C(7) & 110.03(17) \\ C(8)-Si(2)-C(7) & 110.03(17) \\ C(8)-Si(2)-C(9) & 107.31(19) \\ C(8)-Si(2)-C(9) & 103.5(3) \\ C(7)-Si(2)-C(9) & 105.8(3) \\ Si(2)-O(2)-Si(1) & 143.32(13) \\ \end{array}$	Si(1)-C(6)	1.899(3)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Si(2) - O(2)	1 6238(19)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$S_{i}(2) - C(8)$	1 815(4)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Si(2) - C(7)	1 820(5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Si(2) - C(9)	1.906(5)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	O(1) - C(1)	1 183(3)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(1) - C(2)	1.332(3)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(1) - C(4)	1.662(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N(1) - C(3)	1.470(4)
$\begin{array}{c} C(1) - Os - P(2) & 89.30(7) \\ C(1) - Os - P(1) & 89.93(7) \\ P(2) - Os - P(1) & 164.94(2) \\ C(1) - Os - Si(1) & 97.38(2) \\ P(2) - Os - Si(1) & 97.38(2) \\ P(1) - Os - Si(1) & 97.67(2) \\ C(1) - Os - S(1) & 174.09(8) \\ P(2) - Os - S(1) & 90.56(2) \\ P(1) - Os - S(1) & 91.54(2) \\ Si(1) - Os - S(1) & 84.38(2) \\ C(1) - Os - S(2) & 115.53(8) \\ P(2) - Os - S(2) & 83.70(2) \\ P(1) - Os - S(2) & 83.70(2) \\ P(1) - Os - S(2) & 154.72(2) \\ Si(1) - Os - S(2) & 105.43(12) \\ O(2) - Si(1) - C(5) & 105.43(12) \\ O(2) - Si(1) - C(6) & 103.22(12) \\ C(5) - Si(1) - C(6) & 103.26(15) \\ O(2) - Si(1) - Os & 119.78(10) \\ C(6) - Si(1) - Os & 119.78(10) \\ C(6) - Si(2) - C(7) & 110.03(17) \\ C(8) - Si(2) - C(9) & 107.31(19) \\ C(8) - Si(2) - C(9) & 105.8(3) \\ Si(2) - O(2) - Si(1) & 143.32(13) \\ \end{array}$	$C(1) \cap C(2)$	80.50(7)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	C(1) = Os = P(2)	89.50(7)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	C(1) = OS = P(1) P(2) = OS = P(1)	89.93(7)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	P(2) = OS = P(1)	164.94(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	C(1) = OS = SI(1)	89.75(8)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	P(2) = OS = SI(1)	97.38(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	P(1) = Os = Si(1)	97.67(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	C(1) = OS = S(1)	1/4.09(8)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	P(2) = Os = S(1)	90.56(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	P(1) = Os = S(1)	91.54(2)
$\begin{array}{ccccc} C(1) - Os - S(2) & 115.33(8) \\ P(2) - Os - S(2) & 83.70(2) \\ P(1) - Os - S(2) & 82.97(2) \\ Si(1) - Os - S(2) & 154.72(2) \\ S(1) - Os - S(2) & 70.34(2) \\ O(2) - Si(1) - C(5) & 105.43(12) \\ O(2) - Si(1) - C(6) & 103.22(12) \\ C(5) - Si(1) - C(6) & 103.26(15) \\ O(2) - Si(1) - Os & 109.69(7) \\ C(5) - Si(1) - Os & 119.78(10) \\ C(6) - Si(1) - Os & 119.78(10) \\ C(6) - Si(1) - Os & 113.91(10) \\ O(2) - Si(2) - C(8) & 115.07(17) \\ O(2) - Si(2) - C(7) & 110.03(17) \\ C(8) - Si(2) - C(7) & 114.2(3) \\ O(2) - Si(2) - C(9) & 107.31(19) \\ C(8) - Si(2) - C(9) & 103.5(3) \\ C(7) - Si(2) - C(9) & 105.8(3) \\ Si(2) - O(2) - Si(1) & 143.32(13) \\ \end{array}$	Si(1) - Os - S(1)	84.38(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	C(1) = OS = S(2)	115.53(8)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	P(2) - Os - S(2)	83.70(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	P(1) - Os - S(2)	82.97(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$S_1(1) = O_S = S(2)$	154./2(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$S(1) - O_S - S(2)$	70.34(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	O(2) - Si(1) - C(5)	105.43(12)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	O(2)-Si(1)-C(6)	103.22(12)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	C(5)-Si(1)-C(6)	103.26(15)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	O(2)–Si(1)–Os	109.69(7)
$\begin{array}{cccc} C(6)-Si(1)-Os & 113.91(10) \\ O(2)-Si(2)-C(8) & 115.07(17) \\ O(2)-Si(2)-C(7) & 110.03(17) \\ C(8)-Si(2)-C(7) & 114.2(3) \\ O(2)-Si(2)-C(9) & 107.31(19) \\ C(8)-Si(2)-C(9) & 103.5(3) \\ C(7)-Si(2)-C(9) & 105.8(3) \\ Si(2)-O(2)-Si(1) & 143.32(13) \\ \end{array}$	C(5)–Si(1)–Os	119.78(10)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	C(6)-Si(1)-Os	113.91(10)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	O(2)-Si(2)-C(8)	115.07(17)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	O(2)-Si(2)-C(7)	110.03(17)
O(2)-Si(2)-C(9) 107.31(19) C(8)-Si(2)-C(9) 103.5(3) C(7)-Si(2)-C(9) 105.8(3) Si(2)-O(2)-Si(1) 143.32(13)	$C(8) - S_1(2) - C(7)$	114.2(3)
C(8)-Si(2)-C(9) 103.5(3) C(7)-Si(2)-C(9) 105.8(3) Si(2)-O(2)-Si(1) 143.32(13)	O(2)–Si(2)–C(9)	107.31(19)
C(7)–Si(2)–C(9) 105.8(3) Si(2)–O(2)–Si(1) 143.32(13)	C(8)-Si(2)-C(9)	103.5(3)
Si(2)–O(2)–Si(1) 143.32(13)	C(7)-Si(2)-C(9)	105.8(3)
	Si(2)–O(2)–Si(1)	143.32(13)

Infrared spectra (4000–400 cm⁻¹) were recorded as Nujol mulls between KBr plates on a Perkin–Elmer Paragon 1000 spectrometer. NMR spectra were obtained on a Bruker DRX 400 at 25 °C. ¹H, ³¹C, ³¹P, and ²⁹Si NMR spectra were obtained operating at 400.1 (¹H), 100.6 (³¹C), 162.0 (³¹P), and 79.5 (²⁹Si) MHz, respectively. Resonances are quoted in ppm and ¹H NMR spectra referenced to either tetramethylsilane (0.00 ppm) or the proteo-impurity in the solvent (7.25 ppm for CHCl₃). ³¹C NMR spectra were referenced to CDCl₃ (77.00 ppm), ³¹P NMR spectra to 85% orthophosphoric acid (0.00 ppm) as an external standard, and ²⁹Si NMR spectra to tetramethylsilane (0.00 ppm). Elemental analyses were obtained from the Microanalytical Laboratory, University of Otago.

4.2. Preparation of $Os(SiMe_2OH)Cl(CO)(PPh_3)_2$ (1)

Os(SiMe₂Cl)Cl(CO)(PPh₃)₂ (100 mg; 0.11 mmol) was dissolved in THF (10 ml) containing aqueous sodium hydroxide solution (0.2 M) (0.60 ml; 0.12 mmol) and stirred for 5 min at room temperature. The THF was removed under reduced pressure and dichloromethane (10 ml) then added to extract the compound. The dichloromethane solution was dried using anhydrous magnesium sulfate and filtered. Hexane (10 ml) was added to effect crystallisation of pure 1 as a yellow solid (74 mg, 76%). Anal. Calc. for C₃₉H₃₇ClO₂OsP₂Si: C, 54.89; H, 4.37. Found: C, 54.74; H, 4.34%. IR (cm⁻¹): 1910 v(CO); other bands, 3626w v(OH); 899w, 829, 810. ¹H NMR (CDCl₃, δ): 7.64–7.37 (m, 30H, PPh₃), 2.08 (br s, 1H, SiOH, resonance disappears on addition of s, 1H, SIOH, resonance disappears on addition of D_2O), 0.23 (s, 6H, Si(CH₃)₂). ³¹C NMR (CDCl₃, δ): 9.7 (s (SiCH₃)₂), 128.3 (t', [16] ^{2,4}J_{CP} = 9.6 Hz, *o*-C₆H₅), 130.3 (s, *p*-C₆H₅), 132.3 (t', ^{1,3}J_{CP} = 49.4 Hz, *i*-C₆H₅), 134.5 (t', ^{3,5}J_{CP} = 10.8 Hz, *m*-C₆H₅), 183.2 (t, ²J_{CP} = 9.0 Hz, CO). ³¹P NMR (CH₂Cl₂/CDCl₃, δ): 22.6. ²⁹Si NMR (CH₂Cl₂/CDCl₃, δ): 23.27 (t, ²J_{SiP} = 7.3 Hz).

4.3. Preparation of $Os(SiMe_2OLi)Cl(CO)(PPh_3)_2$ (2)

^tBuLi in hexanes (1.5 M, 78 µl, 0.13 mmol) was added by syringe to a yellow slurry of Os(SiMe₂OH)Cl(-CO)(PPh₃)₂ (100 mg, 0.12 mmol) in Et₂O (20 ml) at 0 °C. The mixture was stirred for 30 min, warmed to room temperature and then stirred until gas evolution ceased (\approx 30 min). The volume of the resulting orange mixture was reduced under vacuum and hexane was added to complete precipitation of the orange product. This orange solid was collected by filtration under N2 and washed with pentane to give 2 (80 mg, 78%). Because of extreme sensitivity towards water satisfactory elemental analyses for 2 were not obtained. Similarly, attempts to record solution NMR spectra for this material always gave data for the reprotonated species, i.e., compound 1. However, a solid state IR spectrum was obtained. IR (cm^{-1}) : 1876s v(CO).

4.4. Preparation of Os(SiMe₂OSiMe₃)Cl(CO)(PPh₃)₂ (3)

^tBuLi in hexanes (1.5 M, 103 µl, 0.16 mmol) was added by syringe to a yellow slurry of Os(SiMe₂OH)Cl-(CO)(PPh₃)₂ (132 mg, 0.15 mmol) in Et₂O (20 ml) at 0 °C. The mixture was stirred for 30 min, warmed to room temperature and then stirred until gas evolution ceased (\approx 30 min). Me₃SiCl (196 µl, 1.50 mmol) was then added and the resulting reaction mixture stirred overnight. The mixture was filtered and the volume of the orange filtrate reduced under vacuum. Hexane was then added to effect precipitation of pure **3** as orange crystals (118 mg, 85%). *Anal.* Calc. for C₄₂H₄₅ClO₂OsP₂Si₂: C, 54.50; H, 4.90. Found: C, 54.64; H, 5.00%. Crystals for X-ray analysis were grown from benzene/hexane and proved to be 0.5 benzene solvates (see Table 1). IR (cm⁻¹): 1892 v(CO). ¹H NMR (CDCl₃, δ): -0.23 (s, 9H, Si(CH₃)₃), 0.27 (s, 6H, Si(CH₃)₂), 7.32-7.61 (m, 30H, PPh₃). ³¹C NMR (CDCl₃, δ): 2.1 (Si(CH₃)₃), 11.3 (Si(CH₃)₂), 128.0 (t', ^{2.4}J_{CP} = 9.0 Hz, *o*-C₆H₅), 130.1 (s, *p*-C₆H₅), 132.4 (t', ^{1.3}J_{CP} = 49.4 Hz, *i*-C₆H₅), 134.8 (t', ^{3.5}J_{CP} = 10.0 Hz, *m*-C₆H₅), 183.5 (t, ²J_{CP} = 8.8 Hz, CO).

4.5. Preparation of Os(SiMe₂OSnMe₃)Cl(CO)(PPh₃)₂ (4)

^tBuLi in hexanes (1.5 M, 175 µl, 0.28 mmol) was added by syringe to a yellow slurry of Os(SiMe₂OH)Cl-(CO)(PPh₃)₂ (224 mg, 0.26 mmol) in Et₂O (40 ml) at 0 °C. The mixture was stirred for 30 min, warmed to room temperature and then stirred until gas evolution ceased (\approx 30 min). Me₃SnCl (78.4 mg, 0.39 mmol) was then added and the reaction mixture was stirred overnight. The reaction mixture was filtered and the volume of the orange filtrate was reduced under vacuum. Hexane was then added to effect precipitation of pure 4 as orange crystals (213 mg, 80%). Anal. Calc. for C42H45ClO2OsP2SiSn: C, 49.64; H, 4.46. Found: C, 49.62; H, 4.76%. Crystals for X-ray analysis were grown from benzene/hexane and proved to be 0.5 benzene solvates (see Table 1). IR (cm⁻¹): 1892 v(CO). ¹H NMR (CDCl₃, δ): 0.02 (s with Sn satellites, ² J_{SnH} = 56.8 Hz, 9H, Sn(CH₃)₃), 0.19 (s, 6H, Si(CH₃)₂), 7.31-7.65 (m, 30H, PPh₃). ³¹C NMR (CDCl₃, δ): -2.90 (Si(CH₃)₂), 11.90 (s with Sn satellites, ${}^{1}J_{SnC} = 435.5$ Hz, Sn(CH₃)₃), 127.9 (t', ${}^{2,4}J_{CP} = 9.0$ Hz, $o \cdot C_6H_5$), 129.8 (s, $p \cdot C_6H_5$), 133.0 (t', ${}^{1,3}J_{CP} = 49.4$ Hz, $i \cdot C_6H_5$), 134.8 (t', $^{3,5}J_{CP} = 10.0$ Hz, *m*-*C*₆H₅), 184.1 (t, $^{2}J_{CP} = 9.6$ Hz, CO). ²⁹Si NMR (CH₂Cl₂/C₆D₆, δ): 13.4 (t, ²J_{SiP} = 6.6 Hz). ¹¹⁹Sn NMR (CH₂Cl₂/C₆D₆, δ): 96.2 (s).

4.6. Preparation of $Os(SiMe_2Cl)(\kappa^2-S_2CNMe_2)(CO)-(PPh_3)_2$ (5)

OsH(κ^2 -S₂CNMe₂)(CO)(PPh₃)₂ (1.00 g, 1.15 mmol) was placed in a 250 ml Schlenk tube and toluene (15 ml) and HSiMe₂Cl (2.19 g, 23.0 mmol) added. The tube was sealed, cooled in liquid nitrogen and then evacuated. After warming to ambient temperature, the sealed tube was shielded with a safety shield (*CAUTION*: pressure increases as reaction proceeds) and heated in an oil bath at 90 °C for 18 h. During this time the yellow solution turned to an orange colour. After cooling, the solvent volume was reduced under vacuum and hexane added slowly to induce crystallisation of a pale yellow

solid. This was collected and recrystallised from dry dichloromethane–hexane to give pure **5** (1.04 g, 93%). *Anal.* Calc. for C₄₂H₄₂ClNOOsP₂S₂Si · 1/3CH₂Cl₂: C, 51.62; H, 4.37; N, 1.42. Found: C, 51.62; H, 4.42; N, 1.53%. The single crystal chosen for X-ray analysis proved to be a 1.0 dichloromethane solvate. IR (cm⁻¹): 1888 (s), 1869 v(CO). ¹H NMR (CDCl₃, δ): 0.29 (s, 6H, Si(CH₃)₂), 1.99 (s, 3H, N(CH₃)₂), 2.22 (s, 3H, N(CH₃)₂), 7.30–7.31 (m, 18H, PPh₃), 7.71–7.74 (m, 12H, PPh₃). ³¹C NMR (CDCl₃, δ): 9.8 (Si(CH₃)₂), 36.7, 37.0 (N(CH₃)₂), 127.0 (br, *o*-C₆H₅), 129.3 (s, *p*-C₆H₅), 135.1 (br, *m*-C₆H₅), 188.5 (t, ²J_{CP} = 11.6 Hz, CO), 208.9 (S₂CNMe₂).³¹P NMR (CDCl₃, δ): 8.6 (s).

4.7. Preparation of $Os(SiMe_2OH)(\kappa^2-S_2CNMe_2)(CO)-(PPh_3)_2$ (6)

A solution of Os(SiMe₂Cl)(κ^2 -S₂CNMe₂)(CO)(PPh₃)₂ (550 mg, 0.58 mmol) in a minimum quantity of CH₂Cl₂ was placed on a 10 cm column of silica gel and eluted with acetone. After removal of solvent the resulting crude product was redissolved in a minimum of CH₂Cl₂ and purified by column chromatography on silica gel using acetone/hexane (v/v = 1:3) as eluant. The first colourless fraction was collected and after solvent removal, recrystallisation from CH₂Cl₂-EtOH gave pure 6 as a white solid (450 mg, 83%). Anal. Calc. for C₄₂H₄₃NO₂-OsP₂Si: C, 53.76; H, 4.58; N, 1.49. Found: C, 52.87; H, 4.69; N, 1.63%. IR (cm⁻¹): 1859vs, v(CO), 3643w, v(OH). ¹H NMR (CDCl₃, δ): -0.03 (s, 6H, Si(CH₃)₂), 0.51 (br, 1H, OH, signal disappeared when D₂O was added to the NMR sample), 2.00 (s, 3H, $N(CH_3)_2$), 2.22 (s, 3H, N(CH₃)₂), 7.30–7.34 (m, 18H, PPh₃), 7.70-7.74 (m, 12H, PPh₃). ¹³C NMR (CDCl₃, δ): 6.9 (s, Si(CH₃)₂), 36.7 (s, N(CH₃)₂), 37.1 (s, N(CH₃)₂), 127.1 (t', ${}^{2,4}J_{CP} = 8.0$ Hz, $o-C_6H_5$), 129.0 (s, $p-C_6H_5$), 134.6 (t', ${}^{1,3}J_{CP} = 49.2$ Hz, $i-C_6H_5$), 135.1 (t', $^{3,5}J_{\rm CP} = 9.0$ Hz, $m-C_6H_5$), 189.8 (t, $^2J_{\rm CP} = 11.6$ Hz, CO), 209.3 (s, Me₂NCS₂). ³¹P NMR (CDCl₃, δ): 10.9 (s).

From the second colourless fraction obtained from the chromatography procedure above, $Os(\kappa^2-S_2CNMe_2)Cl(CO)(PPh_3)_2$ was obtained as a white solid, (56 mg, 11%) (see discussion in Section 2.4).

4.8. Preparation of $Os[Si(OH)_3](\kappa^2-S_2CNMe_2)(CO)-(PPh_3)_2$ (7)

Os(SiMe₂Cl)(κ^2 -S₂CNMe₂)(CO)(PPh₃)₂ (140 mg, 0.15 mmol) in THF (15 ml) was treated with KOH (200 mg, 3.6 mmol) in water (1 ml) at ca. 60 °C for 16 h. All volatiles were removed under reduced pressure and the resulting residue was taken up in CH₂Cl₂, dried over anhydrous Na₂SO₄and then filtered. The volume of the filtrate was reduced under vacuum and this mixture placed on a silica gel column. Elution with

a mixture of acetone and hexane (1:3) gave rise to three bands which were collected. The first band contained Os(κ^2 -S₂CNMe₂)H(CO)(PPh₃)₂ in ca. 20% yield. The second band contained Os(SiMe₂OH)(κ^2 -S₂CNMe₂)-(CO)(PPh₃)₂ in ca. 10% yield. From the third band a colourless solid was obtained and recrystallised from CH₂Cl₂/heptane to give pure **7** as colourless microcrystals (50 mg, 36%). *Anal.* Calc. for C₄₀H₃₉NO₄OsP₂S₂. Si · H₂O: C, 49.94; H, 4.30; N, 1.46. Found: C, 50.15; H, 4.15; N, 1.67%. IR (cm⁻¹): 1877 (s) ν (CO). ¹H NMR (CDCl₃, δ): 1.65 (b, 3H, OH), 1.97 (s, 3H, N(CH₃)₂), 2.29 (s, 3H, N(CH₃)₂), 7.32–7.80 (m, 30H, PPh₃). ³¹C NMR (CDCl₃, δ): 36.6 (s, N(CH₃)₂), 36.9 (s, N(C H₃)₂), 127.3 (t', ^{2.4}J_{CP} = 9.0 Hz, *o*-C₆H₅), 129.4 (s, *p*-C₆H₅), 134.2 (t', ^{1.3}J_{CP} = 50.4 Hz, *i*-it C₆H₅), 134.9 (t', ^{3.5}J_{CP} = 9.0 Hz, *m*-C₆H₅), 188.1 (t, ²J_{CP} = 11.6 Hz, CO), 209.5 (s, Me₂NCS₂). ³¹P NMR (CDCl₃, δ): 10.8 (s).

4.9. Preparation of $Os(SiMe_2OSiMe_3)(\kappa^2-S_2CNMe_2)-(CO)(PPh_3)_2$ (8)

А solution of $Os(SiMe_2OH)(\kappa^2-S_2CNMe_2)$ -(CO)(PPh₃)₂ (94 mg, 0.1 mmol) in THF (10 ml) was cooled to ca. -40 °C, and 'BuLi (0.120 ml of a 1.5 M solution in pentane, 0.18 mmol) was added dropwise to this solution. The resulting mixture was allowed to warm to room temperature and stirred for 2 h. Me₃SiCl (0.100 ml, 0.8 mmol) was added and the reaction mixture stirred overnight. All the volatiles were removed under reduced pressure and the residue purified by column chromatography on silica gel. Using CH₂Cl₂ as eluent, a colourless band was collected and the white solid obtained from this band, after recrystallisation from CH₂Cl₂/EtOH, gave pure 8 as colourless crystals (78 mg, 77%). Anal. Calc. for C45H51NO2OsP2Si2: C, 53.50; H, 5.09; N, 1.39. Found: C, 53.53; H, 5.27; N, 1.68%. IR (cm⁻¹): 1861vs, v(CO). ¹H NMR (CDCl₃, δ): -0.18 (s, 9H, Si(CH₃)₃), 0.00 (s, 6H, Si(CH₃)₂), 2.02 (s, 3H, N(CH₃)₂), 2.27 (s, 3H, N(CH₃)₂), 7.28-7.76 (m, 30H, PPh₃). ¹³C NMR (CDCl₃, δ): 2.78 (s, Si(CH₃)₃), 9.20 (s, Si(CH₃)₂), 36.89 (s, N(CH₃)₂), 37.13 (s, N(CH₃)₂), 126.(e, O(CH₃)₂), 0605 (e, N(CH₃)₂), 0706 (s, N(CH₃)₂), 126.9 (t', ${}^{2.4}J_{CP} = 9.4$ Hz, $o-C_6H_5$), 128.9 (s, $p-C_6H_5$), 135.0 (t', ${}^{3.5}J_{CP} = 10.2$ Hz, $m-C_6H_5$), 189.8 (t, ${}^{2}J_{CP} = 12.2$ Hz, CO), 209.8 (s, Me₂NCS₂). ${}^{31}P$ NMR (CDCl₃, δ): 12.1 (s).

4.10. X-ray crystal structure determinations for complexes 3, 4, 5, 6, 7, and 8

X-ray data collection was by Siemens SMART diffractometer with a CCD area detector using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 203 K. Data were integrated and corrected for Lorentz and polarisation effects using SAINT [18]. Semi-empirical absorption corrections were applied based on equivalent reflections using SADABS [19]. The structure was solved by Patterson and Fourier methods and refined by fullmatrix least squares on F^2 using programs SHELXS [20] and SHELXL [21]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located geometrically and refined using a riding model. Compounds 3 and 4 are isostructural and both show disorder between the chloride and carbonyl ligands. These ligands have been refined using half-weighted atoms in the two positions. The final electron density map for compound 6contained numerous electron density peaks, clustered in one region of the unit cell. These could not sensibly be resolved into a molecule and presumably represent a severely disordered heptane molecule. This density was removed using the 'squeeze' function of PLATON [22] before the final refinement. Compound 7 crystallises with a molecule of water. The hydrogen atoms on this water molecule could not be located and are, presumably, disordered. There are a number of hydrogen bonds present in this structure. Two of the hydroxyl groups on the silicon atom form hydrogen bonds to a single sulfur atom on an adjacent molecule and the third hydroxyl group forms a hydrogen bond to the water molecule (see Table 7). Crystal data and refinement details are given in Table 1.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. 241813–241818 for **3**, **4**, **5**, **6**, **7**, and **8**, respectively. Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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